

Lawrence Berkeley National Laboratory

Recent Work

Title

Magnetism of the Alpha-Beta Transition in Solid Oxygen

Permalink

<https://escholarship.org/uc/item/56f2s4b8>

Journal

Chemical Physics Letters, 222(4)

Authors

Silva, A.J.R. da
Falicov, L.M.

Publication Date

1994-02-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

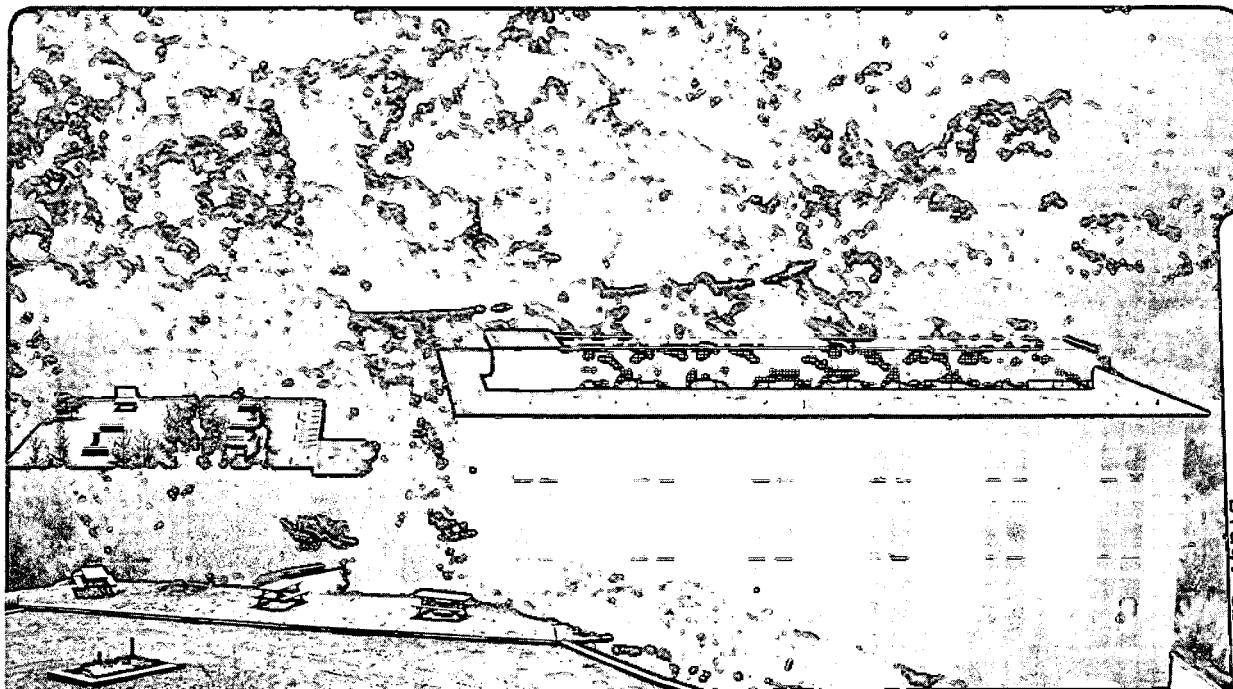
Materials Sciences Division

Submitted to Chemical Physics Letters

Magnetism and the α - β Phase Transition in Solid Oxygen

A.J.R. da Silva and L.M. Falicov

February 1994



REFERENCE COPY
Does Not
Circulate

Bldg. 50 Library

Copy 1

LBL-35211

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

MAGNETISM AND THE α - β PHASE TRANSITION IN SOLID OXYGEN*

Antonio J. R. da Silva and L. M. Falicov

Department of Physics
University of California
Berkeley, CA 94720

and

Materials Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

February 1994

*This work was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

Magnetism and the $\alpha - \beta$ Phase Transition in Solid Oxygen.

Antônio J. R. da Silva and L.M. Falicov

Department of Physics, University of California at Berkeley

and

Materials Sciences Division, Lawrence Berkeley Laboratory,

University of California, Berkeley, California 94720

Abstract

The electronic spectra of α and β solid O_2 were calculated in a full many-body approach for a cluster consisting of four O_2 molecules with *periodic boundary conditions*. Only the partially occupied π orbitals (16 spin-orbitals, 8 electrons) were included. The lowest 81 many-body states, which correspond to neutral, unexcited molecules, describe accurately the magnetic excitations of the solids. The two phases have very different spectra resulting, even at very low temperatures, in a large difference in the (magnetic) entropy. The calculated entropy difference at 23.9 K (the $\alpha - \beta$ phase transition temperature) agrees surprisingly well with the experimentally measured heat of transformation.

The ground state of the oxygen molecule is a spin triplet¹ and, as a consequence, solid O_2 is a molecular crystal with a very rich structure. In particular oxygen is the only known antiferromagnetic, insulating, elemental solid. Therefore, in addition to ordinary low-energy modes characteristic of all van der Waals molecular crystals², i.e., phonons and librations, oxygen exhibits magnetic excitations³⁻⁶ (spin waves or magnons) peculiar to magnetic solids.

At atmospheric pressure the lowest-temperature α -phase of oxygen is monoclinic⁷ and stable⁸ below 23.9 K. It has one molecule per chemical unit cell and space group $C2/m$. The molecules are orientationally ordered^{7,9} and packed in layers with their axes perpendicular to the $a-b$ (layer) planes (see Fig. 2 of Ref. 5). In each plane there are four nearest-neighbor molecules, at a distance of 3.20 Å, and two second-nearest-neighbor molecules, at 3.43 Å. The angle between adjacent nearest-neighbor vectors is 64.4°, and the one between adjacent nearest and second-nearest-neighbor vectors is 57.8°. The molecular spins are aligned along the monoclinic axis $\pm b$, with all nearest neighbors in an antiparallel arrangement to each other^{5,7,10-12}.

Beta oxygen, which is the stable phase⁸ between 23.9 K and 43.8 K, is rhombohedral, with space group $R\bar{3}m$ and one molecule per unit cell. The molecules are also packed in planes with their axis perpendicular to them. These layers are the equivalent of the $a-b$ planes in $\alpha-O_2$, but with six nearest-neighbor molecules at a distance of 3.30 Å and angles of 60°, i.e., a triangular lattice⁵. This arrangement gives rise to "frustration"; that is, there is no possibility of having a classical antiferromagnet and still conserve the lattice symmetry. It is impossible for all nearest-neighbor molecular pairs to align themselves in an antiparallel fashion. Susceptibility measurements^{5,13} indicate a behavior characteristic of antiferromagnets, but no long-range order has been observed by neutron diffraction. There is strong evidence of short-range magnetic order^{10-12,14}. Various models¹⁴⁻¹⁶ have been proposed to explain the magnetic structure of $\beta-O_2$.

The $\alpha-\beta$ first-order transition at 23.9 K has been extensively studied^{12,17-20}. Its origin has been speculated to be either elastic or magnetoelastic. The purpose of this contribution is to establish that the magnetic entropy difference between the two phases is sufficient to

explain, quantitatively, the measured heat of transformation.

All phases of solid O_2 can be viewed as a set of weakly interacting molecules with strong intra-molecular correlations. The dominant (but weak) inter-molecular electronic interactions, therefore, are short ranged. This fact makes solid oxygen an ideal candidate to study its electronic spectra by the so-called small-cluster method²¹. The method treats one-electron and many-body effects on the same footing, but restricts itself to a “small crystal” (a few unit cells with periodic-boundary conditions) or, equivalently, samples reciprocal space in only a few, symmetry-related, selected points in the Brillouin zone. As treated here the method determines accurately the full many-body states of a periodic cluster of four molecules, including excited electronic states of neutral O_2 as well as charge-transfer states. Magnetic interactions and excitations within the present model follow naturally from the many-body electronic structure calculation, and do not have to be introduced *a posteriori* in any way. Therefore, this method should provide a good description, qualitative and quantitative, of the magnetic excitations in α and β oxygen.

Details of the calculation^{22,23} are briefly sketched below. For both $\alpha - O_2$ and $\beta - O_2$ all four molecules in the cluster are in a single $a - b$ plane. Interplane exchange interactions, which are much weaker^{10,12}, are completely neglected. Within the cluster molecules are labelled from 1 to 4. In α -oxygen each molecule, say that labelled 1, has (with periodic boundary conditions included) two each of the molecules 2 and 4 as nearest neighbors, and two of the molecules 3 as second-nearest neighbors. In β -oxygen the six nearest neighbors to molecule 1 are two each of the other molecules, 2, 3, and 4.

Only the partially filled π -orbitals are included explicitly. There are two per molecule, a total of eight in the cluster. The one-particle basis vectors are the mutually orthogonal π_g^- Löwdin spin orbitals of the O_2 molecule, two of each spin on each molecule. With this set of sixteen orbitals and with the eight electrons in the cluster, a total of 12870 many-particle states can be obtained. They are then used to construct the Hamiltonian matrix.

The Hamiltonian is

$$H = \sum_{ij} \sum_{\mu\nu} \sum_{\sigma} t_{ij}^{\mu\nu} c_{i\mu\sigma}^{\dagger} c_{j\nu\sigma} + \frac{1}{2} \sum_{ijkl} \sum_{\mu\nu\epsilon\lambda} \sum_{\sigma\sigma'} U_{ijkl}^{\mu\nu\epsilon\lambda} c_{i\mu\sigma}^{\dagger} c_{j\nu\sigma'}^{\dagger} c_{k\epsilon\sigma'} c_{l\lambda\sigma} \quad (1)$$

Here $t_{ij}^{\mu\nu}$ and $U_{ijkl}^{\mu\nu\epsilon\lambda}$ are one- and two-particle matrix elements, respectively; $c_{i\mu\sigma}^{\dagger}$ ($c_{i\mu\sigma}$) are creation (destruction) operators for an electron in orbital μ (corresponding to π_x or π_y), with spin σ (\uparrow or \downarrow) on site i ($i = 1, 2, 3, 4$). The parameters are obtained from fitting the molecular and solid-state spectra²²⁻²⁴ and include intra-site Coulomb and exchange interactions, inter-site hopping parameters between directed orbitals, crystal field potentials, and inter-site Coulomb interactions.

The Hamiltonian was numerically diagonalized for both phases. Full use was made of group-theoretical techniques that take fully into account space and spin symmetries. The largest symmetry-reduced matrix was (592×592). The complete spectra are very rich, and includes energies up to about 60 eV. For the present purposes only the lowest 81 eigenstates, with energies in the meV range, are relevant. They are shown in Figs. 1 and 2 for α and $\beta - O_2$, respectively. All 81 states, in both cases, correspond to various magnetic arrangements (spin waves) of all neutral molecules in the (${}^3\Sigma_g^-$) electronic ground state.

The two spectra are very different, reflecting the dissimilar magnetic properties of the two phases. Both phases possess a spin singlet ground state, but whereas in $\alpha - O_2$ it is non-degenerate, in $\beta - O_2$ it has a space-group-induced two-fold degeneracy. Moreover, the magnetic excitation spectra are strikingly different. In $\alpha - O_2$ the 81 states are spread over a broad range, with maximum excitation energy of 94 meV, mean energy of 47.9 meV and a standard deviation of 23.0 meV. On the other hand the spin-wave excitation spectrum of $\beta - O_2$ is narrower, and the states, because of the hexagonal symmetry, are highly degenerate. It extends up to 66 meV, has a mean energy of 26.5 meV and a standard deviation of 18.6 meV.

Analysis of spin correlations $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$, for first- and second-nearest neighbors, shows the undisputed antiferromagnetic character of the spin interactions in $\alpha - O_2$. For $\beta - O_2$ there are short-range antiferromagnetic correlations, thus ruling out the possibility of treating beta oxygen as a paramagnet. The results also indicate appreciable quantum fluctuations

and a complex set of states in a “frustrated” Heisenberg-type antiferromagnet.

The spectra from Figs. 1 and 2 have been used to calculate the magnetic contributions to the entropies, $S_\alpha(T)$ and $S_\beta(T)$, associated with the magnetic excitations. The entropy difference $\Delta S_{\beta\alpha}(T) = S_\beta(T) - S_\alpha(T)$ at the transition temperature, $T = T_{\alpha\beta} = 23.9$ K, should give the contribution of the magnetic modes to the heat of transformation. From the data of Figs. 1 and 2 one obtains $T_{\alpha\beta} \Delta S_{\beta\alpha} = 0.95$ meV/molecule, which agrees remarkably well with the experimental value $Q_{\beta\alpha} = T_{\alpha\beta} \Delta S_{\beta\alpha} \simeq 0.97$ meV/molecule obtained for the heat of transition²⁵.

From the experimental observations it is obvious that the α phase has a lower total energy, since it is the stable phase at $T = 0$. The transformation to the β phase can only be driven by (a) a very small total-energy difference between the two phases, and (b) the entropy contribution from the low-lying excited modes. These modes can only be elastic (phonons and librations) or magnetic (magnons or spin waves). The contribution to the heat of transformation at 23.9 K can only thus come from the elastic and magnetic entropies.

The astounding agreement obtained above from the *magnetic entropy alone*, is probably fortuitous, but easy to understand. The small-cluster approach, used in this calculation, does not yield a good description of the long-wave-length excitation modes. It, therefore, may exaggerate the differences between the α and β magnetic entropies, and then account for a larger magnetic share that is the case in reality.

On the other hand, it is very plausible to argue that the *difference* in entropy contributions at 23.9 K from the elastic and librational modes is either negligible or very small. The structures of $\alpha - O_2$ and $\beta - O_2$ are similar. The speeds of sound in both phases²⁵ are almost identical (1645 m/s and 590 m/s for the longitudinal and transverse speeds in the α phase at $T = 23.5$ K; 1633 m/s and 605 m/s in the β phase at $T = 24.5$ K), which should result in negligible entropy difference from the acoustic modes (phonons). The librational modes²⁶ (two modes at 42 cm^{-1} and 72 cm^{-1} in the α phase at $T = 20$ K; a single doubly degenerate mode at 48 cm^{-1} in $\beta - O_2$ at $T = 25$ K) yield at 23.9 K (and assuming an Einstein spectrum for the librations, an overestimate) a contribution of $Q_{\beta\alpha}(\text{librons}) \simeq 0.17$ meV/molecule,

i.e., only an upper limit of 18 percent of the magnetic contribution, as calculated here.

Several important conclusions can be drawn from these calculations:

(A) Both α and β solid oxygen are antiferromagnets, the former a classical one, the latter a "frustrated" one.

(B) "Frustration" causes the spectrum of $\beta - O_2$ to exhibit, in addition to a degenerate ground state, a much lower magnetic excitation energy.

(C) The difference in the magnetic-excitation spectrum is, in turn, responsible for a sizeable difference in magnetic entropy at the transition temperature 23.9 K, sufficient to account for most of the heat of transformation. In other words, the α -to- β first-order transition in solid molecular oxygen is, essentially, driven exclusively by magnetic effects.

ACKNOWLEDGMENTS

This research was supported, at the Lawrence Berkeley Laboratory, by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, U.S. Department of Energy, under contract No. DE-AC03-76SF00098. AJR da S acknowledges support from the Brazilian Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

REFERENCES

- ¹ G. Herzberg, *Spectra of Diatomic Molecules*, (Van Nostrand, Princeton, 1950).
- ² J. D. Wright, *Molecular Crystals*, (Cambridge University Press, Cambridge, 1987).
- ³ E. J. Wachtel and R. G. Wheeler, *Phys. Rev. Lett.* 24 (1970) 233.
- ⁴ I. N. Krupskii, A. I. Prokhvatilov, Yu. A. Freiman and A. I. Érenburg, *Soviet J. Low Temp. Phys.* 5 (1979) 130.
- ⁵ G. C. DeFotis, *Phys. Rev. B* 23 (1981) 4714.
- ⁶ A. P. J. Jansen and A. van der Avoird, *J. Chem. Phys.* 86 (1987) 3583.
- ⁷ C. S. Barrett, L. Meyer, and J. Wasserman, *J. Chem. Phys.* 47 (1967) 592.
- ⁸ H. M. Roder, *J. Phys. Chem. Ref. Data*, 7 (1978) 949.
- ⁹ C. S. Barrett, and L. Meyer, *Phys. Rev.* 160 (1967) 694.
- ¹⁰ P. W. Stephens, R. J. Birgeneau, C. F. Majkrzak and G. Shirane, *Phys. Rev. B* 28 (1983) 452.
- ¹¹ R. J. Meier and R. B. Helmholtz, *Phys. Rev. B* 29 (1984) 1387.
- ¹² P. W. Stephens and C. F. Majkrzak, *Phys. Rev. B* 33 (1986) 1.
- ¹³ H. C. Jamieson and A. C. Hollis Hallet, in: *Proceedings of the 10th. International Conference on Low Temperature Physics*, Moscow 1966, Vol. 4, ed. M.P. Malkov (Viniti Publishing Co. Moscow, 1967) p. 158.
- ¹⁴ F. Dunstetter, V. P. Plakhti and J. Schweizer, *J. Mag. Mag. Mater.* 72 (1988) 258.
- ¹⁵ V. M. Loktev, *Sov. J. Low Temp. Phys.* 5 (1979) 142.
- ¹⁶ A. P. J. Jansen, *Phys. Rev. B* 33 (1986) 6352.
- ¹⁷ Yu. B. Gaididei and V. M. Loktev, *Sov. J. Low Temp. Phys.* 7 (1982) 634.

- ¹⁸ B. Kuchta, T. Luty and R. J. Meier, *J. Phys. C: Solid State Phys.* 20 (1987) 585.
- ¹⁹ R. LeSar and R. D. Eppers, *Phys. Rev. B* 37 (1988) 5364.
- ²⁰ E. Rastelli and A. Tassi, *J. Phys. C: Solid State Phys.* 21 (1988) 1003.
- ²¹ L. M. Falicov, in: *Recent Progress in Many-Body Theories*, Vol. 1, eds. A. J. Kallio, E. Pajanne and R. F. Bishop (Plenum Publishing Corporation, 1988) p. 275.
- ²² A. J. R. da Silva and L. M. Falicov, in: *New Trends in Magnetic Materials and their Applications*, eds. J. L. Morán-López and J. M. Sánchez (Plenum Publishing Corporation, 1994) to appear.
- ²³ A. J. R. da Silva and L. M. Falicov, private communication and to be published.
- ²⁴ R. Bhandari and L. M. Falicov, *J. Phys. C* 6 (1973) 479.
- ²⁵ B. I. Verkin, *Handbook of Properties of Condensed Phases of Hydrogen and Oxygen*, (Hemisphere Publishing Corporation, New York, 1990).
- ²⁶ K. D. Bier and H. J. Jodl, *J. Chem. Phys.* 81 (1984) 1192.

FIGURES

FIG. 1. Spectrum for the lowest 81 states (magnetic excitations) of $\alpha - O_2$. The single, non-degenerate ground-state is indicated by a circle at zero excitation energy.

FIG. 2. Lowest 81 states (magnetic excitations) of $\beta - O_2$. Note that the ground state is doubly degenerate – circle for two states at zero excitation energy – and that there is a singlet excited state at very low energies: 0.80 meV.

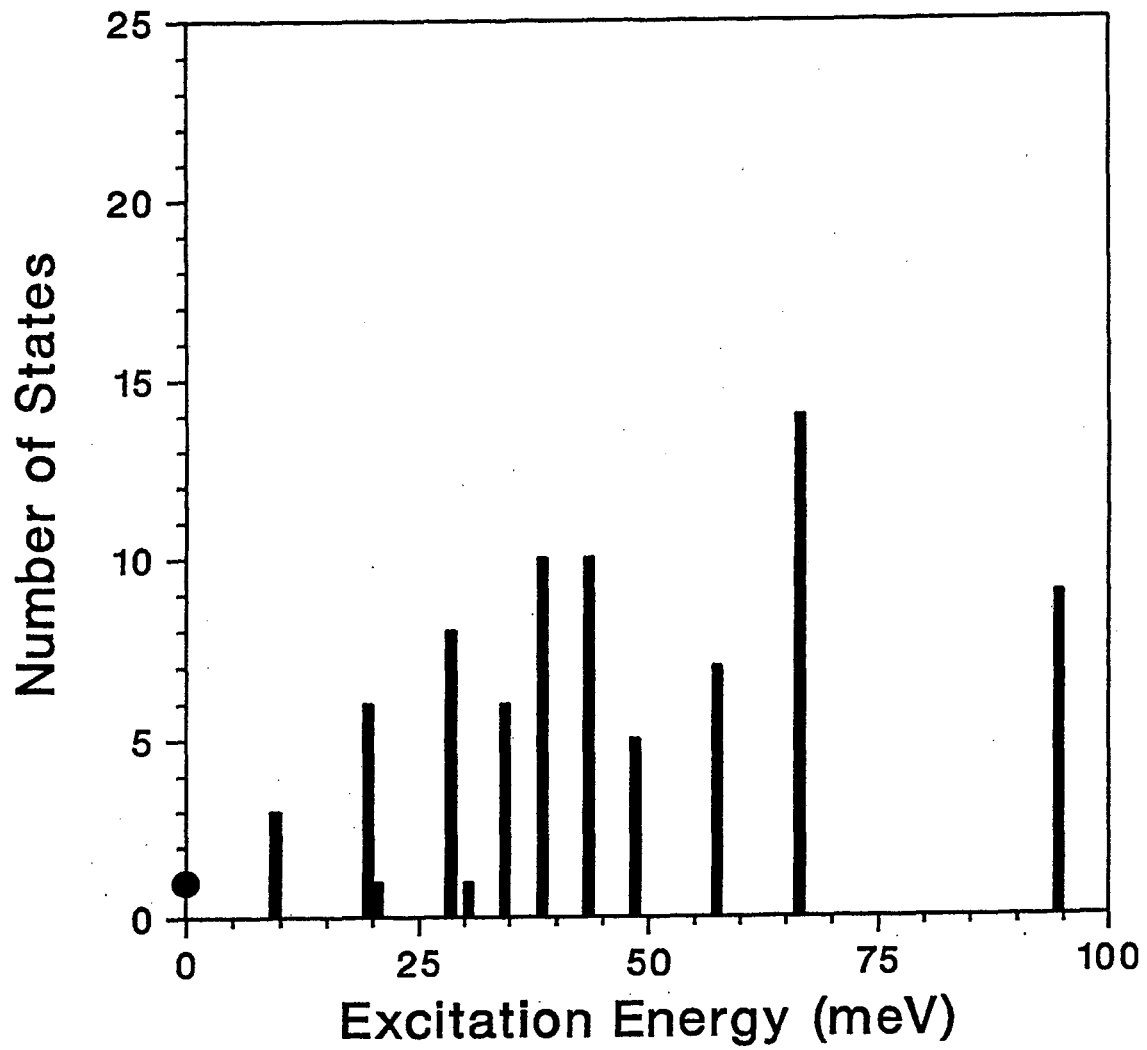


FIGURE 1

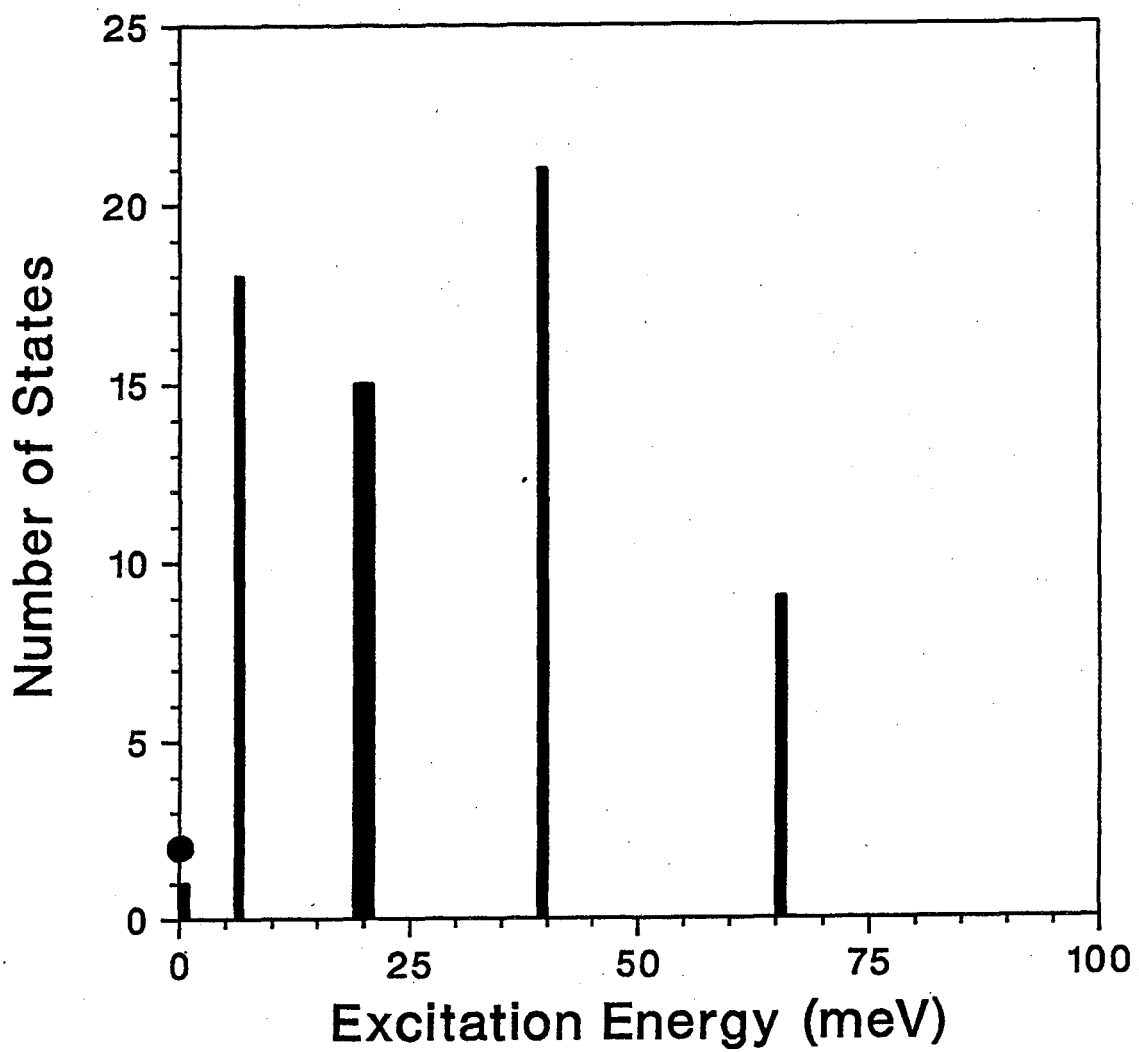


FIGURE 2

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720